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(54) **Fluorescent lamp for use in aquaria**

Fluoreszente Aquariumlampe

Lampe fluorescente pour aquarium

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(56) References cited:
EP-A- 0 364 124
US-A- 4 055 781

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Description

The present invention relates to a fluorescent lamp, and in particular, to a fluorescent lamp for use in aquaria.

Aquaria, particularly the relatively small type for household use, are commonly lit with fluorescent lamps. Former types of fluorescent lamp which have been used, whilst imparting a not unattractive reddish colour to orangy objects such as goldfish, suffers from the disadvantage that, a reddish cast is imparted to almost all colours so that the many varieties of fish now popular for small aquaria do not show up to best advantage. Also there is distortion of green. Furthermore, such types of lamp have the disadvantage of low lumen output, poor lumen maintenance and large colour drift with a affecting colour rendering.

EP-A-0364124 discloses a fluorescent lamp for use in aquaria, the luminescent layer in said lamp comprising a mixture of red, green and blue phosphors, the red phosphor emitting predominantly in the spectral region of from 610 nm to 620 nm, the green phosphor emitting predominantly in the spectral region of from 540 nm to 545 nm and the blue phosphor having a peak emission wavelength between 430 nm and 480 nm with the half peak width not exceeding 80 nm, said red, green and blue phosphors being blended to form said mixture in such proportions that the colour co-ordinates of the lamp employing said mixture on the CIE chromaticity diagram differ from the point x equals 0.300 and y equals 0.232 in any direction by no more than 10 standard deviations of colour matching (SDCM). Most preferably, the lamp of EP-A-0364124 has the colour co-ordinates x equals 0.300 and y equals 0.232.

Individual red, green and blue phosphors which may be used to form the above mixture are well known in the art and according to EP-A-364124 suitable such phosphors include the following:-

Red phosphor

Yttrium and/or gadolinium oxides activated by trivalent europium and having the following formula:

$$(Y_aGd_{1-a})_2O_3:Eu^{3+}$$

In the preferred case a is 1, i.e. the phosphor is:-

$$Y_2O_3:Eu^{3+}$$

Green phosphor

Cerium and terbium activated aluminates, silicates, phosphates and borates selected from compounds of the following formulae:-

$$CeMg\ Al_{11}O_{19}:Tb$$

$$Y_2SiO_5:Ce,Tb$$

$$LaPO_4:Ce,Tb$$

$$LaMgB_5O_{10}:Ce,Tb$$

Particularly suitable are:

$$CeMgAl_{11}O_{19}:Tb \text{ and } LaPO_4:Ce,Tb$$

Blue phosphor

Alkaline earth hexagonal aluminates of the B-alumina structure, or alkaline earth chlorophosphates, each activated by divalent europium and having the following formulae:-

$$BaMgAl_{10}O_{17}:Eu^{2+}$$

$$BaMg_{1.7}Al_{20}O_{32.7}:Eu^{2+}$$

$$BaMg_2Al_{24}O_{39}:Eu^{2+}$$

$$(Sr,Ca,Ba)_{10}Cl_2(PO_4)_6:Eu^{2+}$$

Such a lamp avoids the problems of the former types of fluorescent lamp but uses entirely a mixture of expensive rare-earth phosphors.

The present invention seeks to allow the production of a fluorescent lamp for use in aquaria which avoids or at least reduces the disadvantages described with reference to said former types of lamp whilst allowing a lamp designer to avoid resorting to expensive rare earth phosphors.

According to the present invention, there is provided a fluorescent lamp for use in aquaria, the luminescent layer in said lamp comprising a mixture of phosphors blended in such proportions that the colour coordinates of the lamp on the CIE chromaticity diagram differ from the point x = 0.344 y = 0.302 in any direction by no more than 22 standard deviations of colour matching (SDCM);

the said mixture having a binary mixture of red emitting phosphor emitting predominantly at about 660 nm; and a blue emitting phosphor emitting predominantly in the range 420 to 495 nm with a half peak width in the range 100 to 170 nm; or

a ternary mixture of the said red and blue emitting phosphors and a white emitting phosphor.

The red emitting phosphor may be $Mg_{28}Ge_{7.5}O_{38}F_{10}$ activated by manganese and the white emitting phosphor may be $Ca_5[F,Cl](PO_4)_3$ activated by Antimony (Sb) and Manganese (Mn). Various compounds may be used as the blue emitter.

When the mixture is a binary mixture comprising the red emitting phosphor and the blue emitting phosphor, the blue emitting phosphor emits predominantly in the range 480 to 495 nm with a half peak width in the range 128 to 170 nm. The blue emitting phosphor may be Barium Titanium pyrophosphate or Strontium Fluorophosphate activated with Antimony (Sb).

When the mixture comprises the red emitting phosphor, the white emitting phosphor and the blue emitting phosphor, the blue emitting phosphor emits predominantly in the range 425 to 480 nm with a half peak width in the range 100 to 140 nm, preferably 105 to 136 nm. The blue emitting phosphor may be:

Strontium Pyrophosphate activated by tin having the formula $Sr_2P_2O_7$:Sn ; or
Calcium Fluorophosphate activated by Antimony having the formula

$$Ca_5F(PO_4)_3:Sb\ ;$$

or
Calcium Magnesium Tungstate having the forumula

$$Ca_{(1-x)}Mg_xWO_4$$

where $0 \leq x \leq 1$

For a better understanding of the present invention reference will now be made, by way of example, to the accompanying drawings in which:

FIGURE 1 is the CIE chromaticity diagram showing the colour coordinates of a preferred mixture of phosphors surrounded by an ellipse describing the range of variation of the colour coordinates in accordance with the invention.

FIGURE 2 shows the ellipse of Figure 1 on an enlarged scale.

FIGURE 3 shows a preferred ellipse.

FIGURES 4A, 4B and 4C are spectra of the respective preferred phosphors useful in the present invention.

FIGURE 4D is the spectrum of the preferred mixture of the preferred phosphors useful in the present invention.

FIGURES 5 and 6 are spectra of alternative mixtures of the preferred phosphors useful in the present invention, and

FIGURE 7 is the spectrum of an alternative phosphor useful in yet another alternative mixture of phosphors useful in the present invention.

Referring to FIGURE 1 illustrative fluorescent lamps in accordance with the invention provide a source of light having the colour coordinates falling on and within the ellipse A. A preferred lamp provides light having the colour coordinates B which are

$$x = 0.344 \qquad y = 0.302$$

The ellipse A defines the boundary of all coordinates within about 22 SDCM of coordinates B and is shown enlarged in FIGURE 2. As known to those skilled in the art one SDCM (standard deviation of colour matching) is the least variation in colour noticeable to the human eye. Preferably the ellipse defines the boundary of all coordinates within about 20 SDCM of coordinates B as shown in FIGURE 3.

Line P in FIGURE 1 is the locus of colour coordinates of black body radiation. Line E is the locus of colour coordinates having the same Correlated Colour Temperature as a black body radiator of 4800K. Thus point B has Correlated Colour Temperature equivalent to a black body of temperature 4800K.

Illustrative lamps in accordance with the invention as described in the following EXAMPLES comprise a mixture of two or three phosphors which form the luminescent layer of the lamp. It is necessary to blend the selected phosphors in such proportions that the lamp has the desired colour coordinates shown in FIGURE 1, 2 or 3. The procedure for producing the correct blend is well known to those skilled in the art who readily appreciate that since there are many factors other than weight proportions which affect the contribution of each phosphor in a mixture to the light output and colour of a lamp employing a phosphor layer comprising such a mixture it is not meaningful to lay down a particular weight proportion for each component of the mixture which will result, in all cases, in a lamp having the desired colour coordinates.

These other factors, which cause the required weight properties to vary, include (among other possible ones) particle size profiles of the component phosphors, relative efficacies of the component phosphors, relative bulk densities of the component phosphors, size and loading of lamp using the phosphor mixture.

The phosphors disclosed in the following EXAMPLES are available from GE Lighting Limited, Lincoln Road, Enfield, Middlesex.

EXAMPLE 1 - THE PREFERRED EXAMPLE

A fluorescent lamp for use in an aquarium has a mixture of the following phosphors which forms the luminescent layer of the lamp.

Red Phosphor

Deep red emitting Magnesium Fluorogermanate - activated by manganese.

$$Mg_{28}Ge_{7.5}O_{38}F_{10}:Mn$$

This material, when incorporated in a fluorescent lamp, has a spectrum as shown in Figure 4A with peak red emission at a wavelength of about 660 nm.

Blue Phosphor

Blue emitting, Strontium Pyrophosphate - activated by divalent Tin.

$$Sr_2P_2O_7:Sn$$

This material, when incorporated in a fluorescent lamp has a spectrum shown in FIGURE 4B with peak blue emission at a wavelength of about 460 nm, where the ½ peak width is about 105 nm.

"White" Phosphor

Calcium Halophosphate activated by both Antimony (Sb) and Manganese (Mn), having the formula:-

$$Ca_5[F,Cl](PO_4)_3:Sb,Mn$$

This material emits white light with a colour temperature in the range 3000K to 5500K. It has a spectrum for 4000K as shown in FIGURE 4C, when incorporated in a fluorescent lamp.

Preferred Mixture

The three phosphors are preferably mixed in the ratio by weight

blue	red	white
45	30	25

The preferred mixture when incorporated in a fluorescent lamp has the spectrum shown in FIGURE 4D. The red emission of the red phosphor is apparent around 660 nm and the blue emission of the blue phosphor is apparent around 460 nm. The white phosphor whilst adding to the red and blue emission also adds green emission improving colour rendition and brightness compared to e.g. a lamp comprising only the red and blue phosphors.

The resulting lamp has the colour coordinates B of

x = 0.344 y = 0.302

and provides good colour rendition in aquaria without resort to the expensive rare earth phosphors of EP-A-364121.

EXAMPLE 2

The phosphors of Example 1 may be blended in the ratio

blue	red	white
24	16	60

and, when incorporated in a fluorescent lamp as the luminescent layer, produce a spectrum as shown in FIGURE 5. The lamp produces light having the colour coordinates C x = 0.360 y = 0.345 shown in FIGURE 2 at the edge of the ellipse A.

EXAMPLE 3

The phosphors of Example 1 may be blended in the ratio

blue	red	white
57	38	5

and, when incorporated in a fluorescent lamp as the luminescent layer, produces a spectrum as shown in Figure 6. The lamp produces light having the colour coordinate D x = 0.318 y = 0.258 at the edge of the ellipse A.

ALTERNATIVE EXAMPLES - A1,A2 Binary Mixture of Phosphors

A1) The red phosphor of Example 1 may be blended with

Barium Titanium Pyrophosphate

$$Ba_2TiP_2O_9$$

as a binary mixture.

Barium Titanium Pyrophosphate when incorporated in a fluorescent lamp has a spectrum as shown in FIGURE 7 having a peak emission of about 494 nm with a half peak width of about 170 nm.

The red and blue components are blended in proportions readily ascertainable by those skilled in the art to emit with colour coordinates on or within the ellipse A shown in FIGURE 2 when incorporated as the luminescent layer in a fluorescent lamp.

A2) The Barium Titanium Pyrophosphate of alter-

native A1 may be replaced by

Strontium Fluorophosphate activated with Antimony (Sb):-

$$Sr_5F(PO_4)_3:Sb$$

which has a peak emission of about 485 nm and a half peak width of about 128 nm

ALTERNATIVE EXAMPLES - B)

In Examples 1 to 3, the blue phosphor may be replaced by:

(a) Calcium Fluorophosphate activated with Antimony (Sb)

$$Ca_5F(PO_4)_3 : Sb$$

having a peak emission of about 476 nm and a ½ peak width of about 136 nm; or

(b) Calcium Magnesium Tungstate, which may be activated with lead if desired, having the formula

$$Ca_{(1-x)}\ Mg_x\ WO_4$$

where $0 \leq x \leq 1$

and having: a peak emission in the range 425 - 480 nm and a ½ peak width in the range 105 - 130 nm, depending on the value of x and the extent of lead activation if any, for $0<x<1$; and a peak emission of about 473 nm and a ½ peak width of about 136 nm for $x = 1$.

A selected one of these alternative blue phosphors may be blended with appropriate proportions with the red and white phosphors of Example 1 to produce a mixture which, when incorporated in a fluorescent lamp as the luminescent layer, produces light having the colour coordinates on or within the ellipse A of FIGURE 2.

As will be readily appreciated by those skilled in the art, light having the colour coordinates shown by the ellipse A of FIGURE 2 represents the colour appearance of the light produced by a fluorescent lamp, but will have different colour rendering properties according to the phosphors selected for the mixture. Those skilled in the art will be able to select mixtures of phosphors to produce lamps in accordance with the present invention which produce good colour rendition according to their subjective judgment.

Claims

1. A fluorescent lamp for use in aquaria, the luminescent layer in said lamp comprising a mixture of phosphors blended in such proportions that the colour coordinates of the lamp on the CIE chromaticity diagram differ from the point $x = 0.344$ $y = 0.302$ in any direction by no more than 22 standard deviations of colour matching (SDCM);

   the said mixture having a binary mixture of red emitting phosphor emitting predominantly at about 660 nm; and a blue emitting phosphor emitting predominantly in the range 420 to 495 nm with a half peak width in the range 100 to 170 nm; or

   a ternary mixture of the said red and blue emitting phosphors and a white emitting phosphor.

2. A lamp according to Claim 1 wherein, in said ternary mixture the red emitting phosphor is Magnesium Fluorogermanate activated by Manganese and the white emitting phosphor is a Calcium Halophosphate activated with both Antimony and Manganese.

3. A lamp according to Claim 2 wherein the blue emitting phosphor of the ternary mixture is Strontium Pyrophosphate activated by Tin.

4. A lamp according to Claim 2 wherein the blue emitting phosphor of the ternary mixture is a compound of the formula :

$$Ca_{(1-x)}Mg_xWO_4$$

optionally activated by Lead, where $0 \leq x \leq 1$; or

$$Ca_5F(PO_4)_3$$

activated by Antimony.

5. A lamp according to Claim 3 wherein the blue, red and white emitting phosphors are mixed in the ratio, by weight, 45:30:25 respectively.

6. A lamp according to Claim 1 wherein, in said binary mixture of the red emitting phosphor and the blue emitting phosphor, the said red emitting phosphor is Magnesium Fluorogermanate activated by Manganese and the blue emitting phosphor is Barium Titanium Pyrophosphate or Strontium Fluorophosphate activated with Antimony.

Patentansprüche

1. Fluoreszenzlampe zur Verwendung in Aquarien, wobei die Lumineszenzschicht in dieser Lampe ei-

ne Mischung aus phosphoreszierenden Verbindungen aufweist, die in solchen Verhältnissen gemischt sind, daß die Farbkoordinaten der Lampe auf dem CIE-Farbtondiagramm sich vom Punkt x=0,344 y=0,302 in keine Richtung um mehr als 22 Standardabweichungen bei der Farbabstimmung (SDCM) unterscheiden, die Mischung eine binäre Mischung aus rot emittierender phosphoreszierender Verbindung, die hauptsächlich bei etwa 660 nm emittiert, und blau emittierender phosphoreszierender Verbindung, die hauptsächlich im Bereich von 420 bis 495 nm mit einer halben Peak-Breite im Bereich von 100 bis 170 nm emittiert, aufweist, oder eine ternäre Mischung der roten und der blauen phosphoreszierenden Verbindung und einer weiß emittierenden phosphoreszierenden Verbindung aufweist.

2. Lampe nach Anspruch 1, wobei in der ternären Mischung die rot emittierende phosphoreszierende Verbindung durch Mangan aktiviertes Magnesiumfluorgermanat und die weiß emittierende phosphoreszierende Verbindung sowohl mit Antimon als auch mit Mangan aktiviertes Calciumhalogenphosphat sind.

3. Lampe nach Anspruch 2, wobei die blau emittierende phosphoreszierende Verbindung der ternären Mischung durch Zinn aktiviertes Strontiumpyrophosphat ist.

4. Lampe nach Anspruch 2, wobei die blau emittierende phosphoreszierende Verbindung der ternären Mischung eine Verbindung der Formel:

$$Ca_{(1-x)}Mg_xWO_4,$$

wahlweise aktiviert durch Blei, wobei $0 \leq x \leq 1$, oder

$$Ca_5F(PO_4)_3,$$

durch Antimon aktiviert,
ist.

5. Lampe nach Anspruch 3, wobei die blau, rot und weiß emittierenden phosphoreszierenden Verbindungen in einem Gewichtsverhältnis von 45:30:25 gemischt sind.

6. Lampe nach Anspruch 1, wobei in der binären Mischung aus rot emittierender phosphoreszierender Verbindung und blau emittierender phosphoreszierender Verbindung die rot emittierende phosphoreszierende Verbindung durch Mangan aktiviertes Magnesiumfluorgermanat und die blau emittierende phosphoreszierende Verbindung durch Antimon aktiviertes Bariumtitanpyrophosphat oder Strontiumfluorphosphat sind.

Revendications

1. Lampe fluorescente destinée à être utilisée dans un aquarium, la couche luminescente dans ladite lampe comprenant un mélange de luminophores effectué dans des proportions telles que les coordonnées de couleur de la lampe sur le diagramme de chromaticité CIE ne différent, par rapport au point x = 0,344 y = 0,302 et dans n'importe quelle direction, de plus de 22 écarts types de superposition des couleurs primaires (SDCM);

   ledit mélange comprenant un mélange binaire d'un luminophore émettant du rouge de façon prédominante à environ 660 nm et d'un luminophore émettant du bleu de façon prédominante dans l'intervalle allant de 420 à 495 nm avec une largeur à demi-hauteur comprise dans l'intervalle allant de 100 à 170 nm; ou
   un mélange ternaire desdits luminophores émettant du rouge et du bleu et d'un luminophore émettant du blanc.

2. Lampe selon la revendication 1, dans laquelle, dans ledit mélange ternaire, le luminophore émettant du rouge est un fluorogermanate de magnésium activé par du manganèse et le luminophore émettant du blanc est un halogénophosphate de calcium activé à la fois avec de l'antimoine et avec du manganèse.

3. Lampe selon la revendication 2, dans laquelle le luminophore émettant du bleu est du pyrophosphate de strontium activé par de l'étain.

4. Lampe selon la revendication 2, dans laquelle le luminophore, émettant du bleu, du mélange ternaire est un composé de formule:

$$Ca_{(1-x)}Mg_xWO_4$$

activé facultativement par du plomb, où $0 \leq x \leq 1$; ou

$$Ca_5F(PO_4)_3$$

activé par de l'antimoine.

5. Lampe selon la revendication 3, dans laquelle les luminophores émettant du bleu, du rouge et du blanc sont mélangés selon le rapport , en poids, de 45:30:25 respectivement.

6. Lampe selon la revendication 1, dans laquelle, dans

ledit mélange binaire du luminophore émettant du rouge et du luminophore émettant du bleu, ledit luminophore émettant du rouge est du fluoro-germanate de magnésium activé par du manganèse et le luminophore émettant du bleu est du pyrophosphate de baryum et de titane ou du fluorophosphate de strontium activé par de l'antimoine.

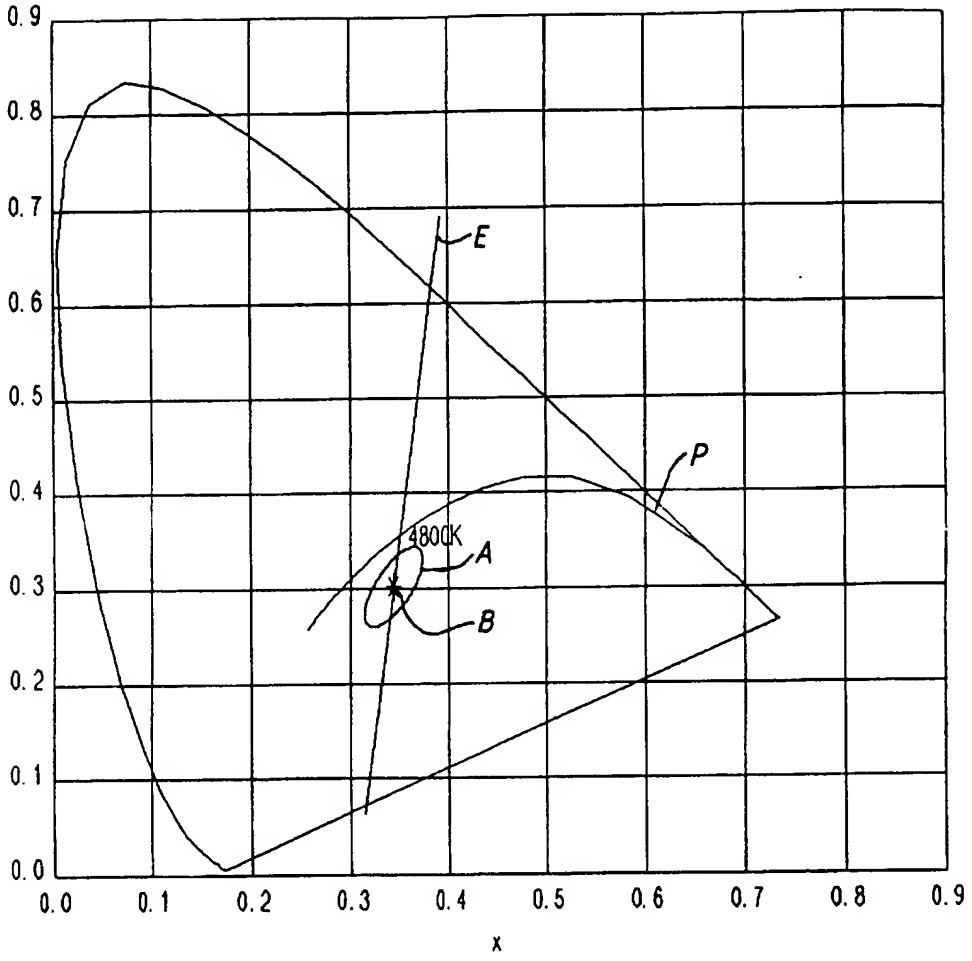
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
x
E
P
4800K
A
B

FIG. 1.

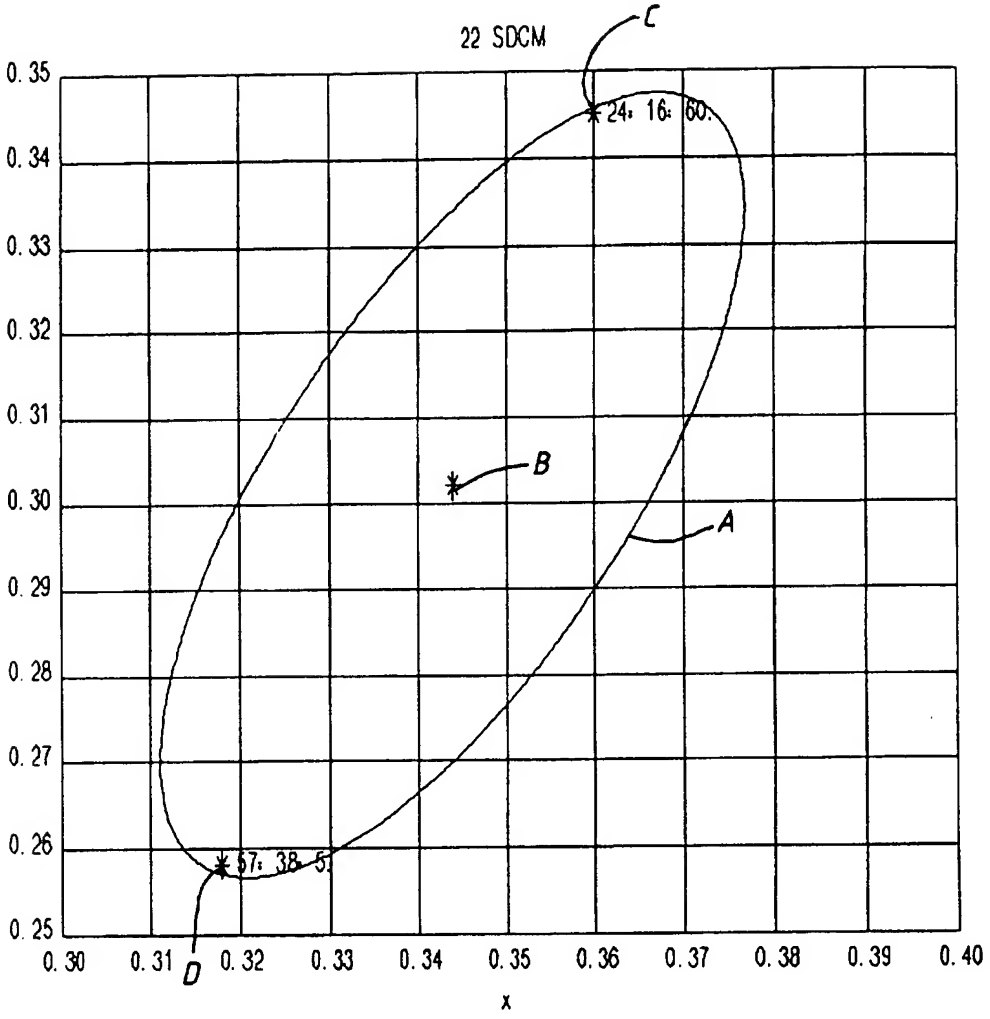
22 SDCM
C
24: 16: 60.
B
A
57: 38: 5.
D
0.35
0.34
0.33
0.32
0.31
0.30
0.29
0.28
0.27
0.26
0.25
0.30
0.31
0.32
0.33
0.34
0.35
0.36
0.37
0.38
0.39
0.40
x

FIG. 2.

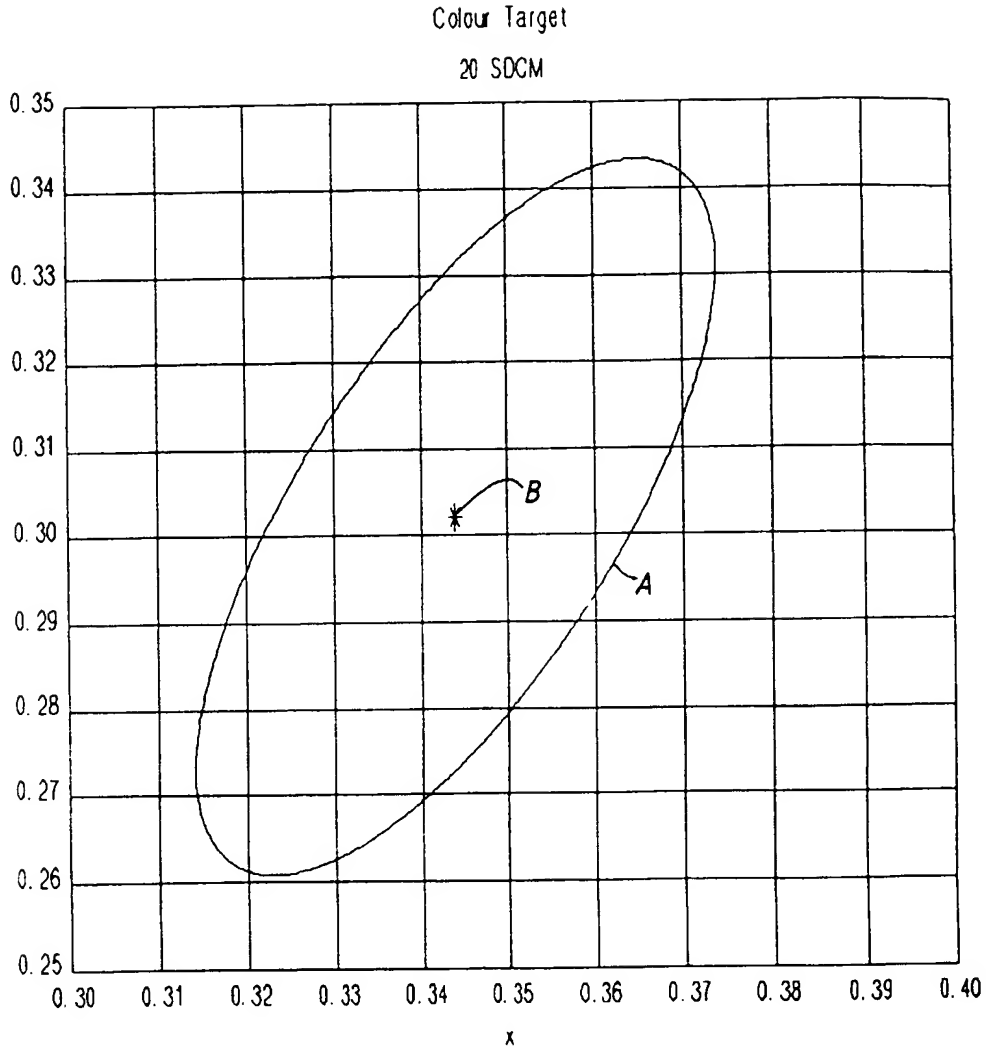
Colour Target
20 SDCM
0.35
0.34
0.33
0.32
0.31
0.30
0.29
0.28
0.27
0.26
0.25
B
A
0.30
0.31
0.32
0.33
0.34
0.35
0.36
0.37
0.38
0.39
0.40
x

FIG. 3.

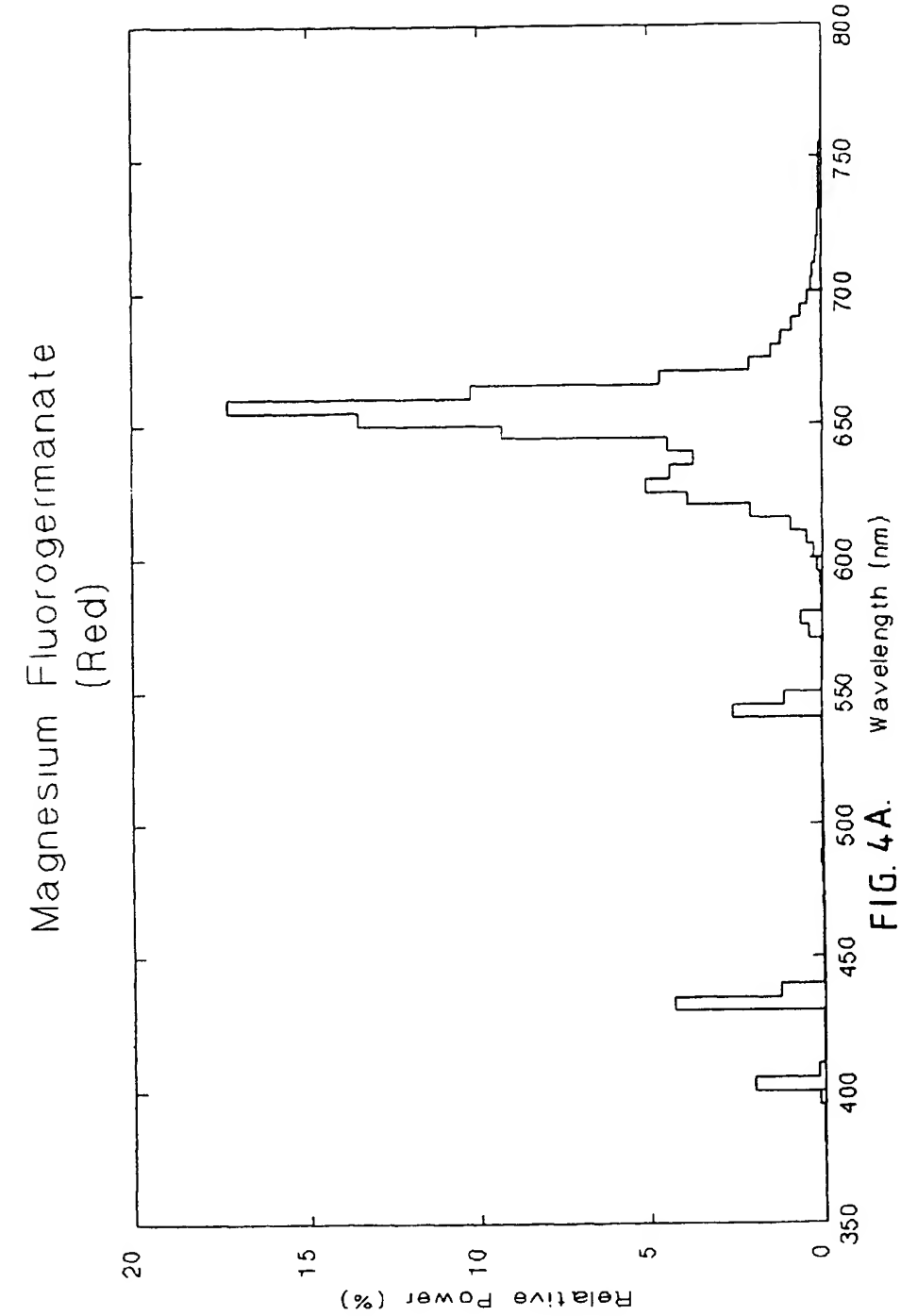
Magnesium Fluorogermanate
(Red)
Relative Power (%)
0
5
10
15
20
350
400
450
500
550
600
650
700
750
800
Wavelength (nm)

FIG. 4A.

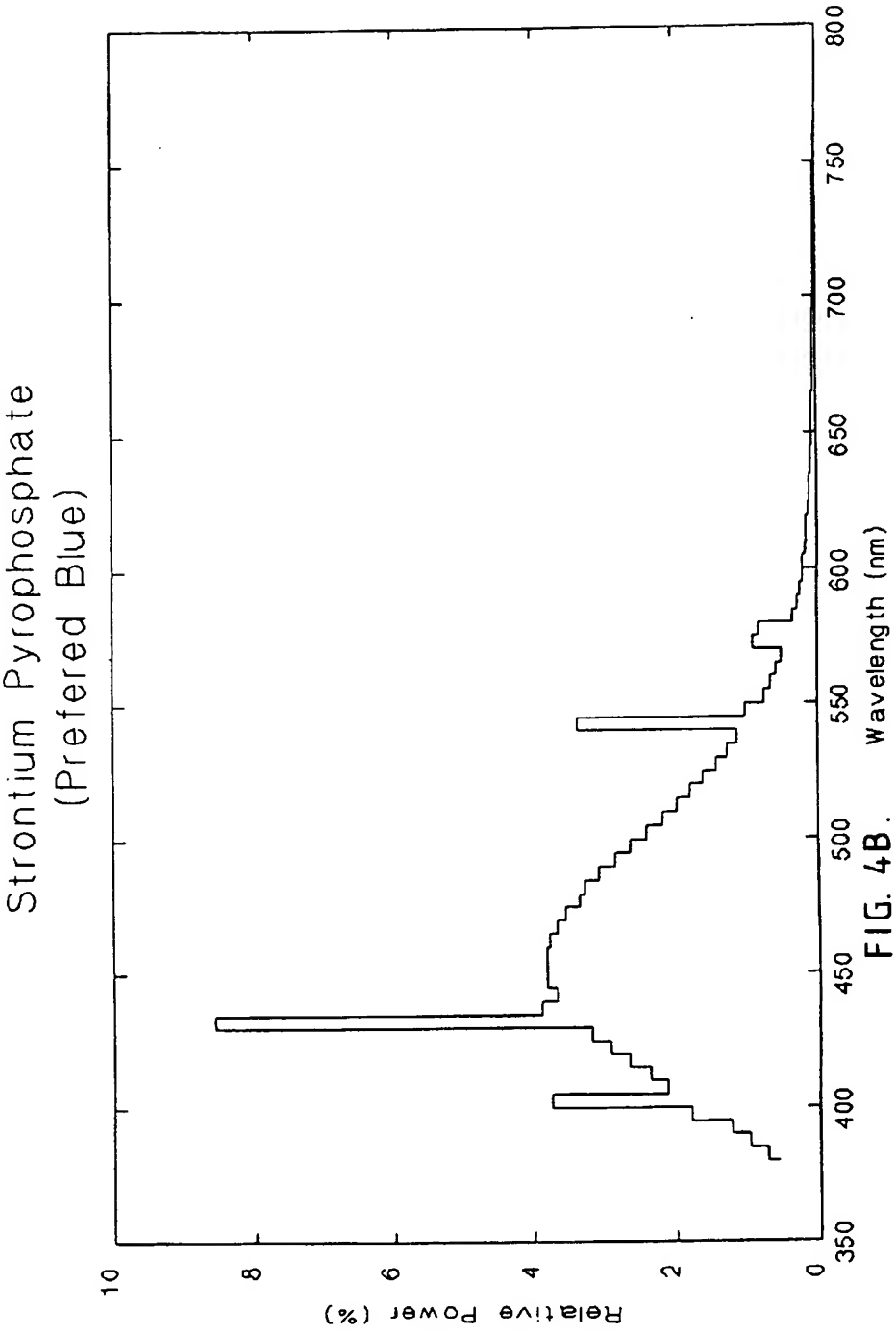
Strontium Pyrophosphate
(Prefered Blue)
Relative Power (%)
0
2
4
6
8
10
350
400
450
500
550
600
650
700
750
800
Wavelength (nm)

FIG. 4B.

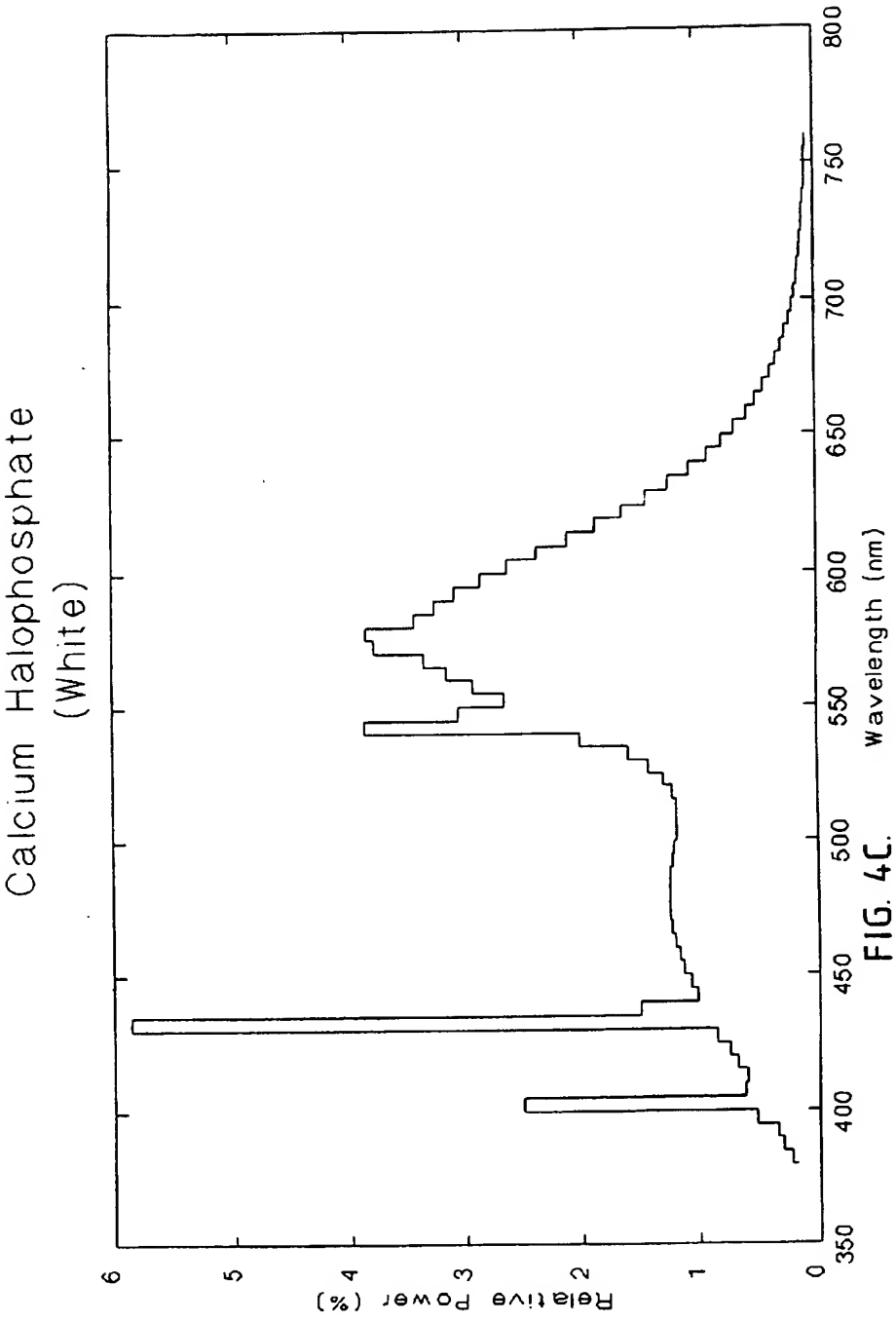
Calcium Halophosphate
(White)
Relative Power (%)
0
1
2
3
4
5
6
350
400
450
500
550
600
650
700
750
800
Wavelength (nm)

FIG. 4C.

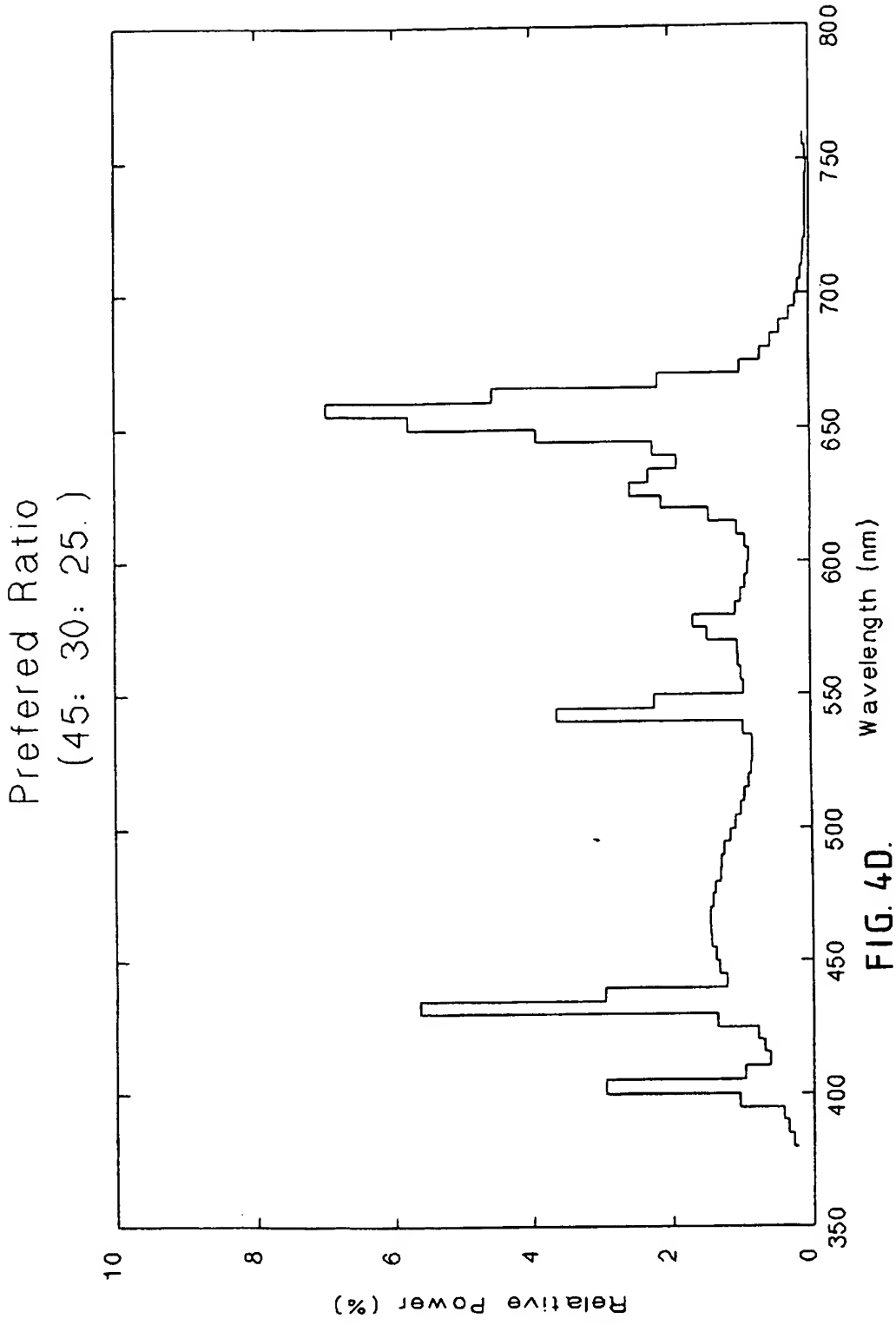
Prefered Ratio
(45: 30: 25)
Relative Power (%)
0
2
4
6
8
10
350
400
450
500
550
600
650
700
750
800
Wavelength (nm)

FIG. 4D.

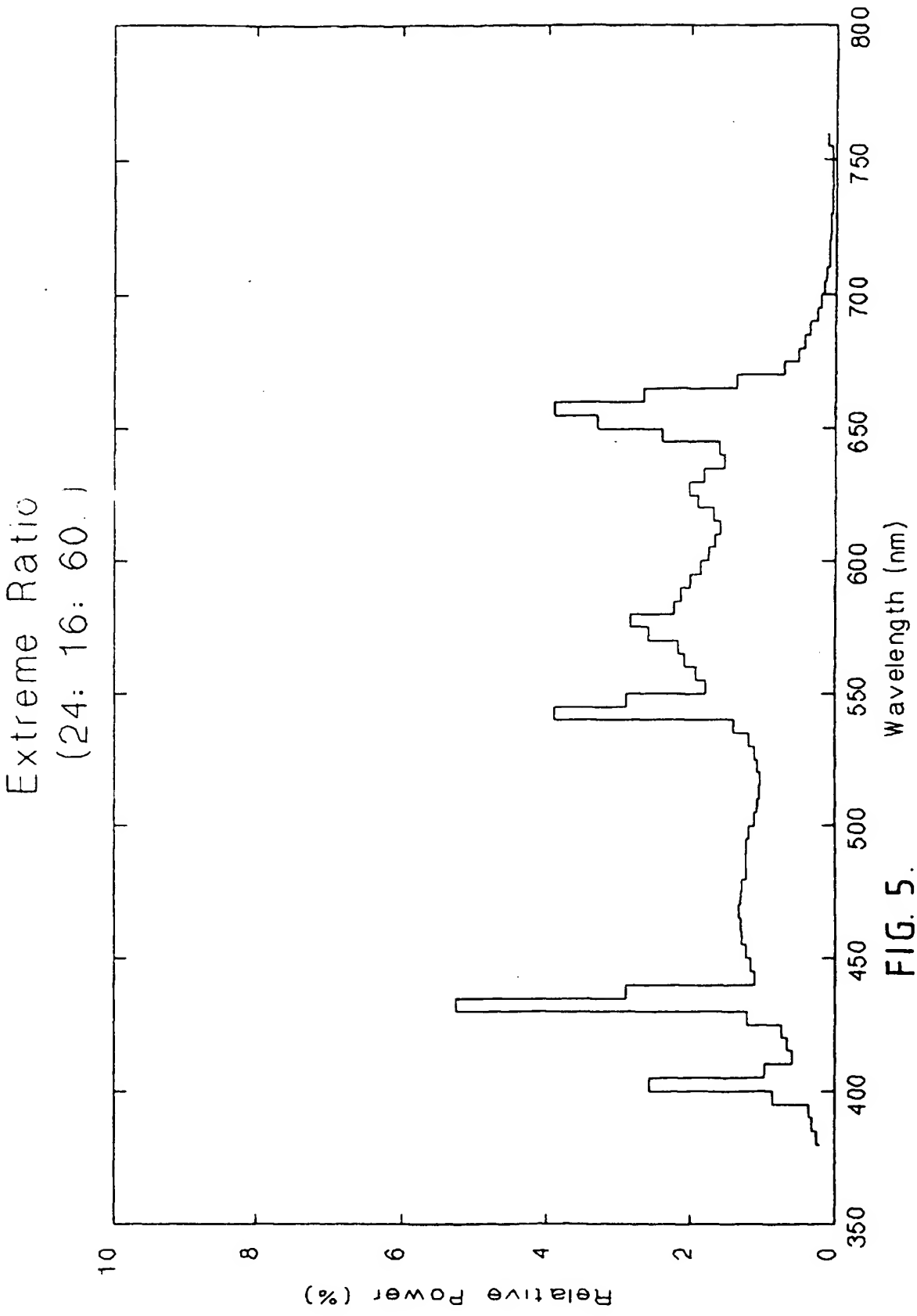
Extreme Ratio
(24: 16: 60)
Relative Power (%)
0
2
4
6
8
10
350
400
450
500
550
600
650
700
750
800
Wavelength (nm)

FIG. 5.

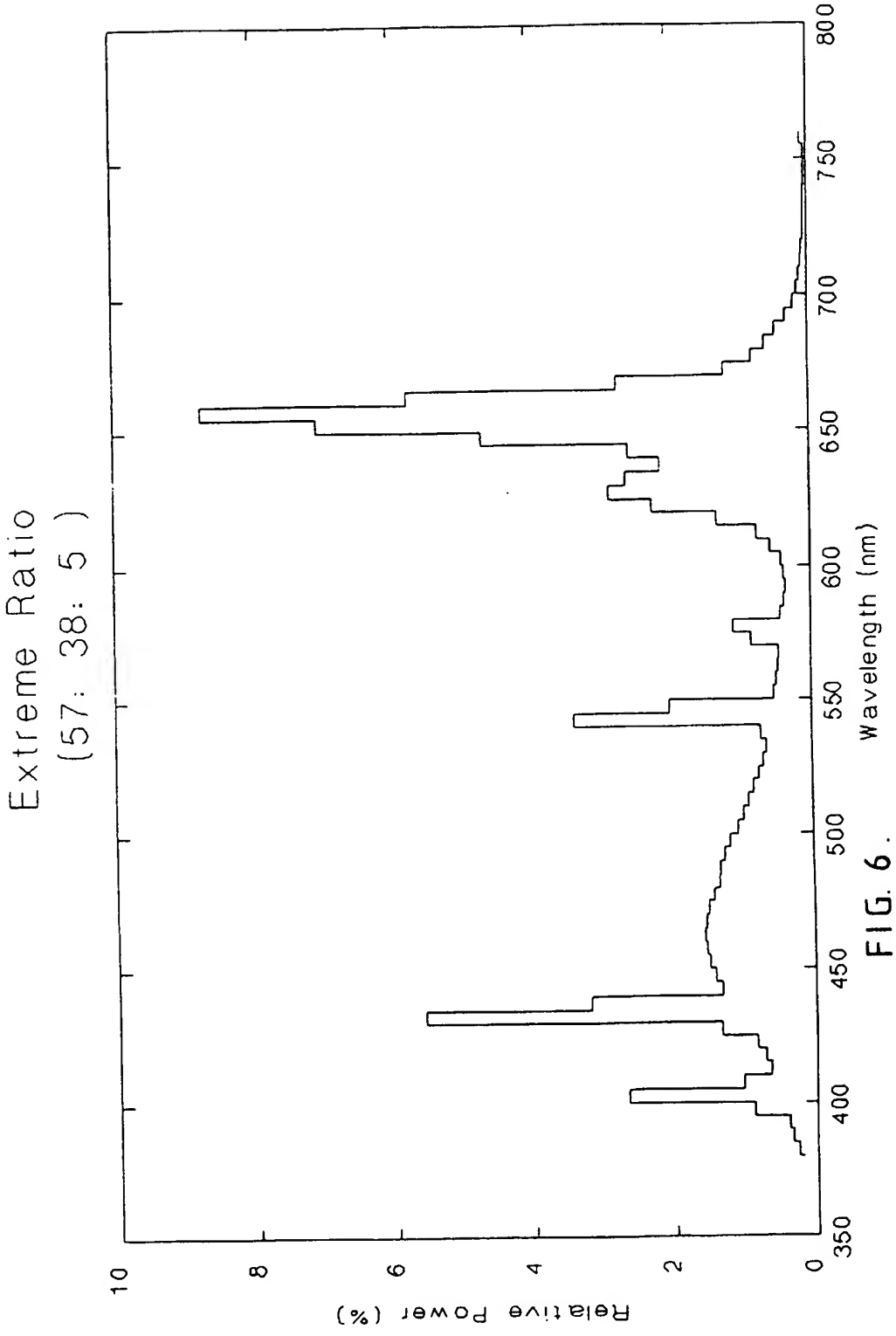
Extreme Ratio
(57: 38: 5)
Relative Power (%)
0
2
4
6
8
10
350
400
450
500
550
600
650
700
750
800
Wavelength (nm)

FIG. 6.

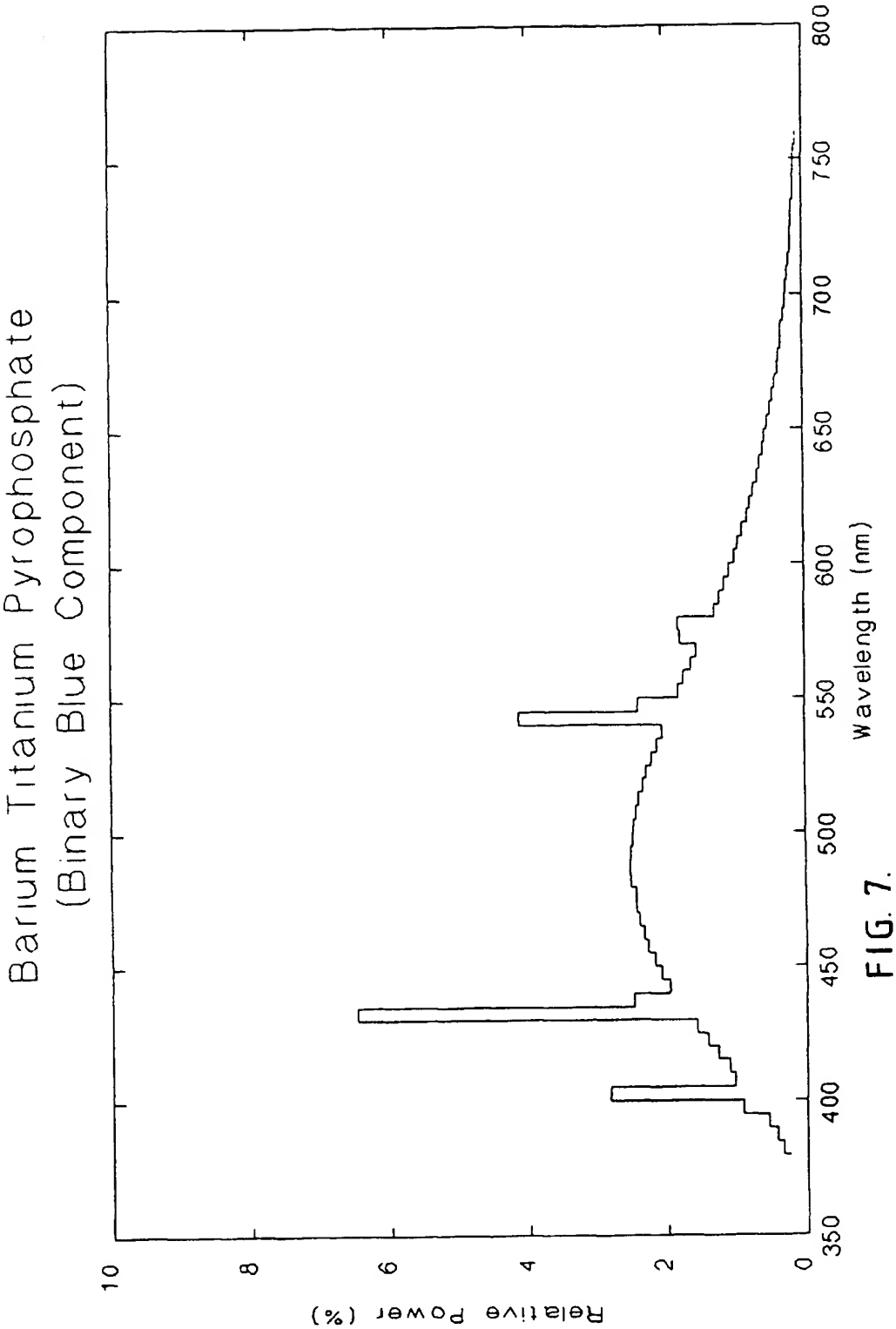
Barium Titanium Pyrophosphate
(Binary Blue Component)
Relative Power (%)
0
2
4
6
8
10
350
400
450
500
550
600
650
700
750
800
Wavelength (nm)

FIG. 7.